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The Action of the Unsymmetrical Ben-
zoylparatolyhydrazine upon
Paraquinones

DISSERTATION

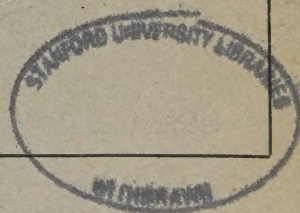
PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

GEORGE WEATHERWORTH STRATTON

COLUMBUS, OHIO

1912



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6. 11. 1911

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A CONTRIBUTION TO THE STUDY OF THE CONSTITUTION OF THE HYDROXYAZO COMPOUNDS; THE ACTION OF THE UNSYMMETRICAL BENZOYLPARATOLYL- HYDRAZINE UPON PARAQUINONES.

The present investigation was undertaken with the prime object of studying the constitution of some parahydroxyazo compounds. Before describing the results, brief references will be made to the more important researches that have been carried out in this field of investigation.

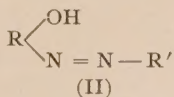
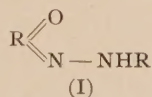
The methods employed for determining the constitution of the hydroxyazo compounds fall into two general classes: namely, (1) those which are purely chemical in their character, and (2) those which are based upon physical chemical measurements. The results obtained by these two methods will be discussed separately.

Chemical Methods.

As the name indicates all hydroxyazo compounds were originally considered to be true derivatives of phenols. Liebermann¹ was the first to question this assumption. Pfaff² had previously observed that when a diazotized aniline solution is added to α -naphthol, the resulting hydroxyazo compound forms at once while with the β -naphthol the compound forms only upon the addition of an alkali. This led Liebermann to the assumption that the compounds derived in this way from α -naphthol and β -naphthol are different in constitution.

Zincke and Bindewald³ found that when phenylhydrazine hydrochloride acts upon α -naphthoquinone in glacial acetic acid solution, an azo-compound is obtained which is soluble in alkalies and identical with benzene-azo- α -naphthol prepared by the action of a diazotized aniline solution upon α -naphthol.

These observations of Liebermann, Zincke and Bindewald led directly to the systematic researches of Goldschmidt and of Meldola. The problem before them was to decide between the following possible structural formulas in which R and R' represent aryl radicals:



If formula (I) correctly represents the constitution of these compounds, then they must be regarded as quinone hydrazones. If formula (II) is the correct one, however, then they are true azo compounds of phenols.

Goldschmidt⁴ studied the action of phenyl cyanate upon these compounds. He found that this reagent combines directly with the parahydroxyazo compounds. He attempted to determine the constitution of these addition compounds and from the results so obtained, to draw conclusions as to the constitution of the hydroxyazo compounds themselves. From a result of these investigations, Goldschmidt concluded that the parahydroxyazo compounds must be regarded as phenol derivatives. The ortho compounds did not form addition products with phenyl cyanate and were therefore classed as quinone hydrazones. These conclusions agreed well with the fact that the para compounds are soluble in alkalies while the ortho compounds are not.

Later when Goldschmidt⁵ in collaboration with Brubacker worked with the acylated hydroxyazo compounds, he changed his view and concluded that the compounds of both series could best be regarded as quinone hydrazones. It seems that the only support for this conclusion is the fact, which he observed, that by the reduction of certain ortho compounds, anilides and orthoamido phenols are formed. This seemed to be a strong argument in favor of the hydrazone formula for the ortho compounds, but there is very little reason for assuming that the para compounds have the same constitution. Goldschmidt was undoubtedly influenced in arriving at this generalization by the great similarity in properties between the paranitroso phenols, which he regarded as monoximes of quinones, and the hydroxyazo compounds. In opposition to this view of Goldschmidt a number of investigators,^{6, 7, 8} notwithstanding the insolubility of the ortho compounds in alkalies held firmly to the view that all hydroxyazo compounds are phenols.

In his earlier work Goldschmidt concluded that only the para compounds react with phenyl isocyanate. Later, however, while working with Löw Beer⁹ he observed under certain conditions the ortho compounds also react with this reagent. In both series the addition products are insoluble in dilute alkalies. In the ortho series these products upon reduction yield hydroxyazo compounds which undergo the benzidine change and form diacid bases insoluble in dilute alkalies. These facts led the author to again change his view, this time regarding all hydroxyazo compounds as phenols.

Meldola and his students,^{10, 11, 12, 13, 14} working on the reduction

of acylated hydroxyazo compounds, proved that under certain conditions four reduction products are formed. This would seem to indicate that the reduction methods as applied to determining the constitution of these compounds are not of great value. The quinone hydrazone formula for the ortho compounds agreed well with the derived triazine formulas of Meldola and so he accepted it in view of the fact that the bulk of evidence seemed to favor this constitution.

McPherson,¹⁵ under the direction of Nef, undertook the study of the constitution of the hydroxyazo compounds from a new standpoint. He showed that the condensation products of unsymmetrical acylated phenylhydrazines with paraquinones are isomeric with the acylated products of the corresponding parahydroxyazo compounds. The corresponding isomers, however, yield the same compound upon saponification, *viz.*, the parent hydroxyazo compound. With orthoquinones, however, the condensation products formed with the unsymmetrical acylated phenylhydrazines are not isomeric but identical with the acylated derivatives of the corresponding orthohydroxyazo compounds. These results can best be explained on the assumption that the orthohydroxyazo compounds are quinone hydrazones.

McPherson's investigations definitely prove the constitution of the acyl derivatives of the parahydroxyazo compounds. They do not absolutely prove the constitution of the parent hydroxyazo compounds, although they naturally indicate that those of the para series are true azo compounds while those of the ortho series are quinone hydrazones.

This work has been extended¹⁶ to the naphthylhydrazines and in the present investigation to the tolylhydrazines with the same general results. McPherson's view was commonly accepted after publication of his first research, but the work of Hewitt and his collaborators which directly followed pointed to an opposite conclusion in the case of the ortho compounds. Hewitt^{21, 22, 23, 24, 25, 26} drew his conclusions from a study of the action of nitric acid and bromine upon the hydroxyazo compounds. This same line of work had been carried out previously by several investigators.^{17, 18, 19, 20} The general results have been to show that dilute nitric acid and bromine, in the presence of sodium acetate and acetic acid, when acting upon the para compounds are substituted in the ring in the ortho position to the hydroxyl group. This is a characteristic reaction of true phenols and hence indicates that the para compounds are true hydroxyazo bodies. The action of nitric acid in the presence of

concentrated sulphuric acid is somewhat different, and led the author to assume that while under most conditions the para compounds have the constitution indicated by their name, in the presence of concentrated sulphuric acid they exist as salts of the tautomeric quinonehydrazone.

From a study of the reaction of benzeneazocoumaric acid, Mitchell²⁷ concludes that the parahydroxyazo compounds are phenol derivatives and not quinone hydrazones.

Smith and Mitchell²⁸ made a careful study of the action of diazomethane and mercuric acetate upon the hydroxyazo compounds with a view of obtaining additional information in regard to their constitution. These reagents are very active and not likely to produce tautomeric changes. Diazomethane acts upon the para compounds forming oxygen-methyl-ethers such as are obtained by direct alkylation. The authors regard this as proof of the phenolic constitution of the para compounds since a quinone hydrazone under the same conditions should give a nitrogen ether. The ortho compounds are not acted upon by diazomethane. This fact, however, can not be taken as proof of the absence of the hydroxyl group because diazomethane is not an infallible reagent for detecting this group. The non-activity here might be due to steric hindrance.

Dimroth²⁹ has shown that amines and phenols react readily with mercuric acetate, the mercuric acetate complex entering the ring in the ortho or para position with respect to the hydroxyl or amino groups. These results appeared to Smith and Mitchell²⁸ to offer a satisfactory method for determining the constitution of the hydroxyazo compounds. They found that mercuric acetate acts in the same general way upon hydroxyazo compounds of both the ortho and para series and conclude that "the identical behavior of ortho- and parahydroxyazo compounds with mercuric acetate must be conditioned by similarity of structure, and the compounds of the ortho series must therefore be of the azo type since all evidence, chemical or physical, proves that the para compounds are not quinone hydrazones." In more recent times these same authors³⁰ have extended this work with mercuric acetate into the naphthalene series.

Jacobson and Hönigsberger³¹ prepared the metahydroxyazo benzene which had hitherto been unknown, and made an extensive study of this compound and its relation to the other two isomers. It was chiefly through a comparison of the properties of these compounds that the authors assigned to the para derivatives the phenolic constitution. That the ortho compounds are hydrazones is not

convincingly shown though the comparisons made would point to this conclusion.

The investigations of Borsche on the relation of the quinone-hydrazones to the parahydroxyazo compounds are of the utmost importance and give a great deal of convincing information. In his first work³² he prepared and studied a series of quinone-phenyl-carbamic hydrazones. He was led to the study of these compounds because of the belief that the parahydroxyazo compounds would probably exist in the isomeric hydrazone form when the azo group is linked to two dissimilar groups. The results of his experiments indicate that the condensation products of quinones and carbamic hydrazids are not hydrazones but parahydroxyazo derivatives. It also seems that the hydrazones have a tendency to change into hydroxyazo compounds and not the reverse. The azoformanilide compounds studied possess, to a rather high degree, the properties of quinone derivatives, thus showing the influence of the groups combined to the azo group. The condensation products of quinones with formyl, hyppuryl and benzolhydrazine behave as hydroxyazo compounds.³³

Borsche³⁴ has also studied the condensation products of quinone oximes with acylated hydrazines of the type $\text{NH}_2\text{NH.COR}$ and $\text{NH}_2\text{NR.COR}$. In a more recent work³⁵ he found that phenyl hydrazine containing negative substituted groups react with para quinones forming the corresponding hydroxyazo derivatives. Thus ortho-nitrophenylhydrazine reacts with benzoquinone forming the parahydroxyazo compound ($\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{OH}$) which is identical with the compound obtained by coupling diazotized ortho-nitroaniline with phenol.

Willstätter and Veraguth³⁶ converted some of the benzoquinone-phenylhydrazones into the isomeric hydroxyazo compounds and thus demonstrated the labile character of the acyl group.

Möhlau and Kegel³⁷ found that the condensation product of benzene azo- α -naphthol and methyl-diamino-benzhydrol upon reduction gave acetanilide as one of the products. From this they concluded that the para compounds are hydrazones. Auwers and Eisenlohr³⁸ repeated this work but obtained aniline and not acetanilide as one of the reduction products. Later, Möhlau³⁹ confirmed the work of Auwers and Eisenlohr.

Oddo and Puxeddu^{40, 41, 42} have studied the hydroxyazo compounds extensively, but their work has been almost entirely in the ortho series.

Physical Chemical Methods.

The chief investigators who have adopted physical chemical methods in the study of this problem are Auwers and Orton, Hantzsch and Tuck.

Auwers and Orton⁴³ hoped to throw some light upon the question by a study of the cryoscopic measurements of these compounds in naphthalene solution. They thought that inasmuch as phenolic compounds behave abnormally in this respect the hydroxyazo compounds should behave similarly in case they are true phenols. In the para series the measurements are all abnormal while in the ortho series they are normal. The authors also studied the effect of the nature and position of different groups in the ring on the cryoscopic measurements. They safely concluded that the para compounds are true phenols, but that the facts in the case of the ortho series are not sufficiently convincing to say, without reserve, that these compounds are quinone hydrazones. In fact Auwers¹⁹ later verified his conclusions with regard to the para compounds, but did not hold to the belief that the ortho compounds are hydrazones.

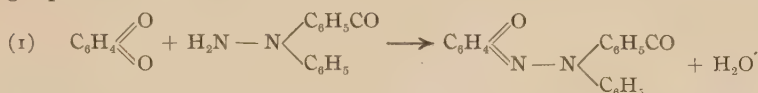
Hantzsch in collaboration with Farmer⁴⁴ studied the problem from the standpoint of the conductivity measurements of the free compounds and their sodium salts. He concluded that all the hydroxyazo compounds of both series are, in the free condition, quinone hydrazones. They are, however, "pseudo acids" and so can form salts of hydroxyazobenzene of the following formula: $\text{NaO.C}_6\text{H}_4\text{.N : NC}_6\text{H}_5$. The proof of the evidence of these pseudo acids is not given and Hantzsch later expressed the view that the hydroxyazo compounds may be more safely designated as phenols. More recently still while working on the relation of color to constitution by optical methods he concluded⁴⁵ that the free parahydroxyazo compounds possess a constitution similar to their ethers, that is, they are true phenols.

Tuck and his collaborators^{46, 47, 48} made a careful and extensive study of the absorption curves of dilute solutions of the hydroxyazo compounds and their derivatives. The comparison of a large number of these curves led the authors to the following conclusions: The parahydroxyazo compounds, their ethers and benzoyl derivatives possess the azophenol configuration; this is also true for the ethers of the ortho-compounds while it is probable that the benzoyl derivatives of the latter are quinonehydrazones. These results of Tuck are criticized by Auwers and others on the grounds that the differences exhibited by the various curves are not sufficient to justify the

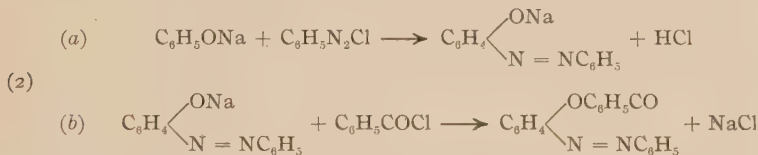
conclusions drawn. In a later communication Tuck⁴⁷ points out the fact that his critics have overlooked the important factor of the different dilution of the solutions used.

Theoretical.

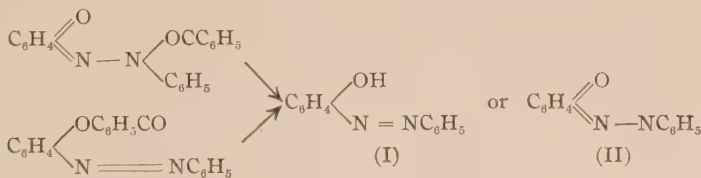
McPherson,¹⁵ working under the direction of Nef, has shown that unsymmetrical benzoylphenylhydrazine condenses with para-quinones forming the corresponding quinonehydrazones. For example with benzoquinones the reaction is represented by the following equation:



The resulting hydrazones proved to be isomeric with the benzoyl derivatives of the corresponding hydroxyazo-compounds. For example the hydrazone obtained by the action of unsymmetrical benzoylphenylhydrazine on benzoquinone according to equation (1) given above is isomeric with the benzoyl derivative of hydroxyazobenzene, prepared by the reaction expressed in the following equations:

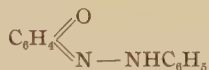


Now both the isomeric benzoyl derivatives formed as represented in equations (1) and (2) given above, yield on saponification the same compound, namely, hydroxyazobenzene (benzeneazophenol). The reactions are represented by the following equations:

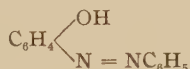


It is evident, therefore, that in the saponification of one of the compounds a migration of the hydrogen atom takes place. If the migration takes place in the hydrazone, the hydrogen atom which takes the place of the benzoyl group passing from the nitrogen to the oxygen, then the constitution of the resulting hydroxyazobenzene must be represented by formula I. On the other hand if the migration takes place in the benzoyl derivative of hydroxyazobenzene then

formula II correctly represents the constitution of the parent compound. From the general results obtained by different investigations, it seems probable that the migration actually takes place in the hydrazone and that formula I is the correct one for hydroxyazobenzene. This indicates that the molecule represented by the formula

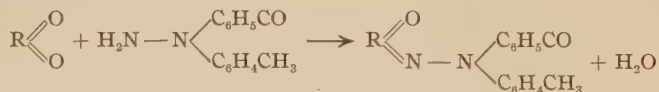


is unstable, rearranging as fast as formed to the more stable form:

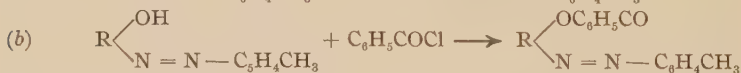
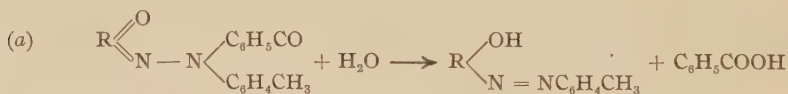


It was thought that by varying the radicals it might be possible to

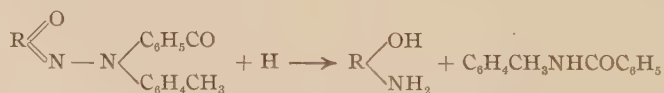
obtain a stable body of the general formula $\text{R} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} \text{—NHR}'$. If such a compound could be isolated, it would throw much light upon the general question of the constitution of the hydroxyazo compounds. In the present investigation, I studied the action of the unsymmetrical benzoylparatolyldiazine upon some of the paraquinones and have found that they react according to the following general equations:



The resulting hydrazones when saponified yield hydroxyazo compounds, and these when benzoylated give derivatives that are isomeric with the original benzoyl hydrazones:



Upon reduction the benzoyl hydrazones break down as shown in the following equation:

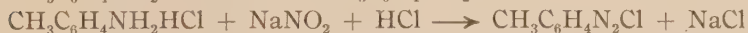


Experimental Part.

PREPARATION OF PARATOLYLHYDRAZINE.

Paratolyldiazine is somewhat unstable and hence was prepared

as needed. It is most readily obtained from paratoluidine by methods similar to those used in preparing phenylhydrazine from aniline. The following method gave good results and was used in this investigation. To 18 grams of paratoluidine were added 150 cc. of water and then 30 cc. of hydrochloric acid (sp. gr. 1.2). The resulting mixture was then heated until all of the toluidine dissolved. In some cases it was not necessary to apply heat, the rapid addition of the acid liberating sufficient heat to dissolve the solid. The resulting clear liquid was poured into a large beaker (1000 cc.) and stirred rapidly until it was sufficiently cool to be placed in a freezing mixture. It was then stirred continuously and when the temperature fell to 5° the theoretical quantity of sodium nitrite (12 grams) dissolved in about 50 cc. of water was gradually added through a dropping funnel. The temperature was not allowed to rise above 5° during the addition of the nitrite. To the diazo solution still in the freezing mixture there was added, slowly at first and with constant stirring, 120 grams of stannous chloride dissolved in 100 cc. of concentrated hydrochloric acid. The tolylhydrazine hydrochloride separated out as a thick, white solid. It was filtered off by suction and the filtrate salted out to obtain the hydrochloride which remained in solution. The yield of the hydrochloride was from 65 to 75 per cent. of the theoretical amount. In order to obtain the free tolylhydrazine the hydrochloride was neutralized with sodium hydroxide. This was accomplished by transferring the solid to an evaporating dish, adding a small quantity of water (100–200 cc.) and then solid sodium hydroxide. The hydroxide was added slowly with constant stirring of the mixture and the addition stopped temporarily when the action became too violent. The tolylhydrazine separated out on the surface of the liquid as a yellow oil which solidified to an almost white solid when the solution cooled. The solid formed a crust on the surface of the liquid and was skimmed off while the remaining solution was extracted with ether in order to dissolve out any remaining hydrazine. The crude tolylhydrazine was purified by recrystallizing from ether. The reactions may be represented as follows:



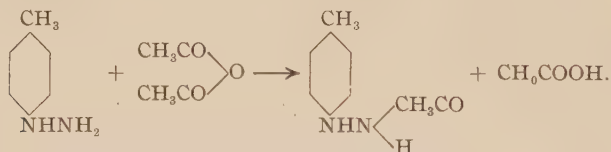
PREPARATION OF β -ACETYLPARATOLYLHYDRAZINE.

This compound was first prepared by Gattermann, Johnson and

Hölze.⁴⁹ They dissolved the tolylhydrazine in glacial acetic acid and boiled the resulting solution for several hours. Upon standing, the acetyl compound crystallized from the acetic acid. I have prepared it by two different methods, both of which gave good results. In the first of these the solid tolylhydrazine was placed in an Erlenmeyer flask and the theoretical amount of acetic anhydride slowly added. To prevent decomposition the temperature was kept down by allowing cold water to flow over the outside of the flask. The acetyl compound formed at once. It was purified by crystallizing from hot water.

The second method of preparing the acetylhydrazine was used to great advantage when the tolylhydrazine was prepared as given above and ethereal solutions of it obtained. To the ethereal solution of the tolylhydrazine, acetic anhydride was added slowly until the addition of a few drops ceased to cause a violent boiling of the ether. During the course of the reaction decomposition was prevented by the rapid evaporation of the ether. Before the required amount of acetic anhydride was added the acetylhydrazine began to separate and at the end of the experiments a large quantity of it had settled to the bottom of the vessel. This was filtered from the ether and washed once or twice with ether, a procedure which obviated the troublesome recrystallization from hot water. The acetyl compound which remained dissolved in the ether was recovered by crystallizing from water.

β -Acetylparatolylhydrazine is a white solid, soluble in all the ordinary organic solvents excepting ligroin. Its preparation is represented by the following equations:



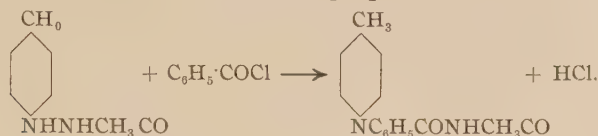
It is quite soluble in boiling water but very insoluble in cold water. From this solvent it crystallizes in white leaflets melting at 130°. An analysis for nitrogen gave the following result:

0.3099 gram gave 47 cc. moist N at 19° and 740 mm.
Calculated for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}$: N, 17.07. Found: N, 16.88.

α -BENZOYL- β -ACETYLPARATOLYLHYDRAZINE.

Upon benzoylating β -acetylparatolylhydrazine in benzene solu-

tion by means of benzoyl chloride the benzoyl group enters in the α -position as shown in the following equation:



In carrying out the reaction the acetyl compound was dissolved in benzene (about 25 grams per 250 cc. of benzene) in a flask which was then connected with a reflux condenser. The theoretical quantity of benzoyl chloride was added through the condenser and the solution boiled until hydrogen chloride ceased to be given off. The reaction was complete after about three hours' boiling. The addition of benzoyl chloride often caused the formation of a precipitate which dissolved, however, when the mixture was heated.

If the benzene solution is allowed to cool slowly the α -benzoyl- β -acetylhydrazine separates out as a hard cake which adheres firmly to the bottom of the flask. It was found better to pour the hot solution into a beaker, evaporate a portion of the benzene and cool rapidly, constantly agitating the liquid. In this way it was obtained in the form of finely divided crystals. The yield was almost quantitative.

α -Benzoyl- β -acetylparatolylhydrazine is very slightly soluble in ligroin, rather more soluble in ether and alcohol and chloroform, and very soluble in benzene. It may be purified by crystallizing from benzene or benzene-ligroin. From these solvents it is obtained in compact nodules of small crystals, which melt sharply at 135° .

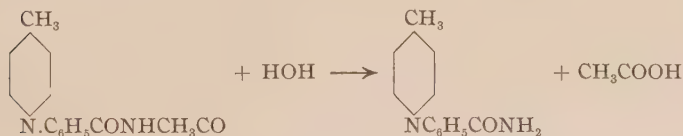
0.3044 gram gave 28.8 cc. moist N at 21° and 744.2 mm.

0.2106 gram gave 0.5533 gram CO_2 and 0.1131 gram H_2O .

Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$: N, 10.45; C, 71.64; H, 5.97.

Found: N, 10.48; C, 71.66; H, 5.96.

α -BENZOYLPARATOLYLHYDRAZINE-SULPHATE.



The saponification represented in the above equation was accomplished by the action of dilute sulphuric acid upon the compound dissolved in alcohol. By this means it was thought possible to tell when the reaction was completed since under these conditions benzoic ether is formed. It was found that the formation of benzoic ether served as a fair though not accurate indication that all of the

acetyl group had been removed. By the use of sulphuric acid, however, the sulphate of the benzoyl compound was formed and this served better than the free compound in the formation of the condensation products with quinones.

To 25 grams of α -benzoyl- β -acetylparatolyldiazine dissolved in 200 cc. of 95 per cent. alcohol were added 150 cc. of water. The flask containing the solution was then connected with a reflux condenser, 3 to 4 cc. more than the theoretical amount of sulphuric acid added, and the mixture boiled until the odor of benzoic ether was noticeable. After evaporating off a part of the alcohol and allowing the solution to cool the sulphate crystallized out. It was always found to be mixed with a greater or less quantity of unchanged α -benzoyl- β -acetylparatolyldiazine. Different concentrations of sulphuric acid were tried with the idea of eliminating this difficulty, but the most satisfactory results were obtained with the dilution given. Too long boiling and excess of sulphuric acid tended to convert the compounds into free tolyldiazine.

The sulphate as obtained by the method given was purified by washing it with chloroform and ether. It is a white solid rather insoluble in all organic solvents excepting alcohol. It may be crystallized from aqueous solutions of this solvent.

α -BENZOYLPARATOLYLHYDRAZINE.

This compound is readily formed upon neutralization of the sulphate. The sulphate was dissolved in dilute alcohol, carefully neutralized with sodium carbonate or sodium bicarbonate and the resulting solution extracted with ether. Upon evaporation of the ether an oil was obtained which could be made to crystallize only after repeated trials. The crystallization was finally brought about by extracting the oil several times with ligroin, combining the ligroin extracts and evaporating them slowly. The compound usually separated first in the form of an oil, but on standing for several days changed almost entirely into fine white crystals which were grouped together in nodules resembling very much the α -benzoyl- β -acetylparatolyldiazine. They were purified by washing rapidly with ether.

The free α -benzoyl compound is very soluble in organic solvents. It melts at 68–70°.

0.3083 gram gave 34 cc. moist N at 21° and 752 O.

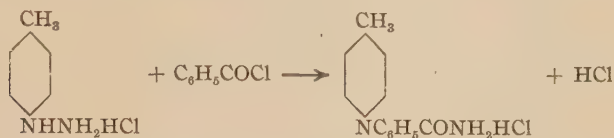
0.2052 gram gave 0.1155 gram H₂O and 0.5560 gram CO₂.

Calculated for C₁₄H₁₄N₂O: N, 12.39; C, 74.34; H, 6.19.

Found: N, 12.32; C, 73.9; H, 6.25.

α -BENZOYLPARATOLYLHYDRAZINEHYDROCHLORIDE.

Several attempts were made to prepare this compound directly from tolylhydrazine hydrochloride. It was thought that possibly the hydrogen chloride combined to the hydrazine might protect the β -position and thus allow the benzoyl group to enter in the α -position as expressed in the following equation:

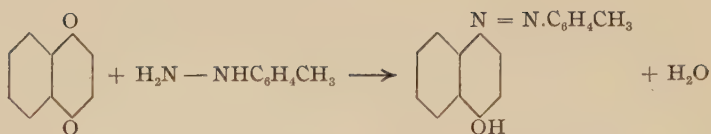


The general method used consisted in treating the tolylhydrazine hydrochloride with an excess of benzoylchloride and boiling the solution for a few minutes. A large volume of water was then added and the solution boiled again to convert the benzoyl chloride into benzoic acid. The solution was next neutralized with sodium carbonate and extracted with ether. Upon allowing the ethereal solution to stand, a white solid crystallized out. It melted at 180° and did not give the tests for the free benzoyl compound. It was probably a dibenzoyl derivative. The hydrochloride was very readily prepared from the free compound by dissolving the latter in benzene and then passing in dry hydrogen chloride. It separated out as a pinkish white solid which was easily purified by washing with benzene and ether. By heating the compound from 70 – 80° it sublimed, forming white needles melting at 175° . It was not determined whether the sublimation product was the hydrochloride or a decomposition product.

THE ACTION OF TOLYLHYDRAZINE UPON PARAQUINONES.

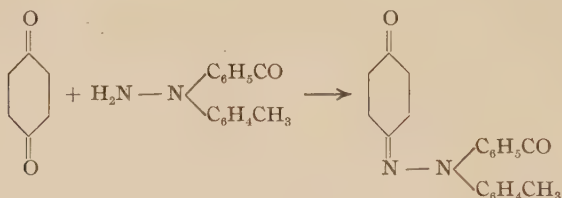
It has long been known⁵⁰ that phenylhydrazine acts as a reducing agent upon quinones of the benzene series converting them into the corresponding hydroquinones. With α -naphthoquinone, on the other hand, condensation takes place and a hydroxyazo compound is produced. It was found that tolylhydrazine acts similarly. Thus by its action in benzene solution, benzo-, tolu- and thymoquinones were converted into the corresponding hydroquinones, while α -naphthoquinone gave tolueneazo- α -naphthol. In the first three cases nitrogen was evolved and the hydroquinones were precipitated after the solution had stood for some time. With the α -naphthoquinone, precipitation took place at once.

The reaction with α -naphthoquinone is represented by the following equation:



BENZOQUINONE- α -BENZOYLPARATOLYLHYDRAZONE.

The sulphate or hydrochloride of the alpha substituted tolylhydrazine condenses with benzoquinone, yielding the corresponding hydrazone:



As in the case of the similar compound prepared from α -benzoylphenylhydrazine¹⁵ the reaction is best carried out in dilute alcoholic solution, since in concentrated solution decomposition results.

One gram of benzoquinone was dissolved in 200–250 cc. of 95 per cent. alcohol. Water was added to this solution until the total volume was about 600 cc. To this solution was then added a slight excess above the theoretical amount of α -benzoylparatolylhydrazine sulphate (3.5 grams) dissolved in 600 cc. of dilute alcohol of the same strength as the solvent for the quinone. The sulphate solution was prepared in the same way as the quinone solution. The mixture was allowed to stand for 24 hours.

The hydrazone separated out as a yellowish solid which settled to the bottom of the flask. It was filtered by suction, dried on the hot plate at 100° and recrystallized several times from benzene-ligroin and finally from ligroin. It was thus obtained in the form of finely divided, yellow crystals which melted at 141°. The yield of the crude product was 3 grams. The compound is soluble in ether, alcohol, benzene and chloroform and slightly soluble in ligroin.

0.3099 gram gave 26 cc. moist N at 21.8° and 719 mm.

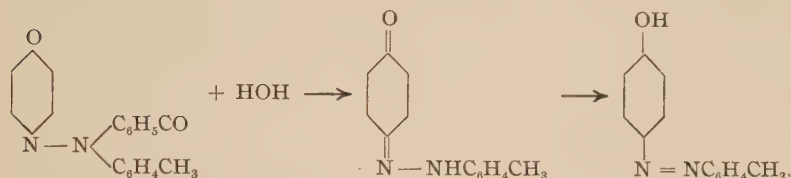
0.1973 gram gave 0.5475 gram CO₂ and 0.0900 gram H₂O.

Calculated for C₂₀H₁₆N₂O₂: N, 8.86; C, 75.95; H, 5.06.

Found:

N, 8.95; C, 75.63; H, 5.07.

ACTION OF SAPONIFYING AGENTS UPON BENZOQUINONE- α -BENZOYL-
PARATOLYLHYDRAZONE.



Upon saponification with hot alcoholic potash or concentrated sulphuric acid the hydrazone was converted into an hydroxyazo compound and benzoic acid as shown in the above equation. Sulphuric acid was found to be a more convenient saponifying agent than alcoholic caustic potash. The hydrazone was dissolved in an excess of concentrated sulphuric acid and then poured into a large volume of water which caused the separation of the hydroxyazo compound. It was usually more or less impure when obtained in this way and was purified by dissolving it in a 20 per cent. sodium hydroxide solution, filtering, and neutralizing the filtrate with hydrochloric acid. Further purification was accomplished by repeated recrystallization from ligroin and benzene-ligroin. The finely divided orange-yellow crystals thus obtained melted sharply at 152° . This compound was found to be identical with paratolueneazophenol prepared by the method given below.

PREPARATION OF TOLUENEAZOPHENOL AND ITS BENZOATE.

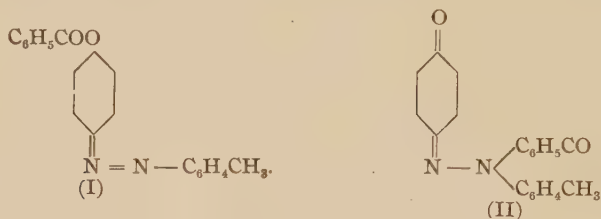


Paratolueneazophenol was prepared^{51, 52, 53} as represented in the equation by the action of diazotoluene chloride upon phenol. The solution of diazotoluene chloride was added to an alkaline solution of phenol. The resulting solution was then neutralized with hydrochloric acid and the azo compound which separated out purified by crystallizing from ligroin. From this solvent beautiful orange-red monoclinic crystals were obtained which melted sharply at 152° . That this compound is identical with the one resulting from the saponification of benzoquinone- α -benzoylparatolylhydrazone was shown by melting-point determinations of a mixture of the pure crystals of these two compounds. The melting point remained at 152° .

The benzoate of this hydroxyazo compound was prepared⁵⁶ by

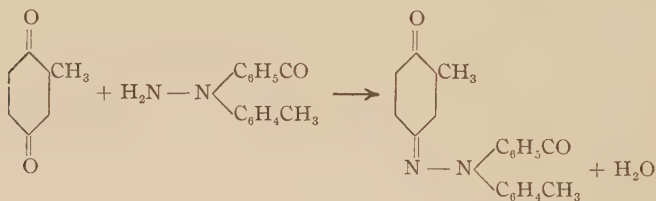
the Baumann-Schöten reaction. The compound was dissolved in a 20 per cent. solution of sodium hydroxide and an excess of benzoyl chloride added. Warming the solution caused the separation of the benzoate as an oil which solidified when the solution cooled. After filtering and washing several times with boiling water it was dried on the hot plate and recrystallized from ligroin. Beautiful orange-red needle-shaped crystals resulted which melted sharply at 159° .

This benzoate, according to its method of preparation, should be represented by formula I below. It is isomeric and not identical with the corresponding benzoylhydrazone, the constitution of which is represented by formula II below. This was shown by melting-



point determinations of the two compounds and mixtures of them. The melting point of the mixture was not sharp and was considerably lower than that of either of the components. The colors and crystalline forms of the two compounds are also different.

TOLUQUINONE- α -BENZOYLPARATOLYLHYDRAZONE.



This condensation was effected under exactly the same conditions that were used in the preparation of the benzoquinonehydrazone.

One gram of toluquinone was dissolved in 250 cc. of 95 per cent. alcohol and water added until the total volume was about 700 cc. To this solution was then added 3 grams of α -benzoyl-paratolylhydrazine-sulphate dissolved in about 700 cc. of dilute alcohol (3 parts of 95 per cent. alcohol to 4 parts of water). The hydrazone began to separate at once and at the end of 24 hours the reaction was completed. Two grams of the crude product were obtained. Purification was effected by repeated recrystallization from ligroin and benzene-ligroin. The fine yellow crystals obtained melted at

178°. They are somewhat lighter in color than the crystals of benzoquinone hydrazone. The hydrazone is very slightly soluble in dilute alcohol. It is not very soluble in ligroin but dissolves readily in other organic solvents.

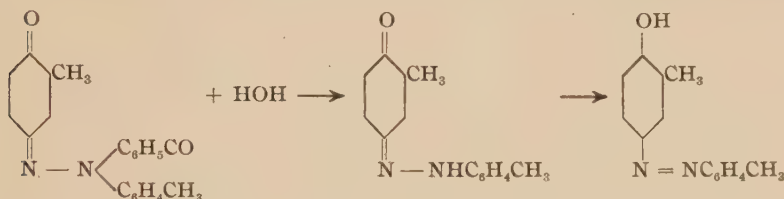
0.4836 gram gave 37 cc. moist N at 20° and 745 mm.

1970 grams gave 0.5502 gram of CO₂ and 0.0980 gram H₂O.

Calculated for C₂₁H₁₈N₂O₂: N, 8.49; C, 76.37; H, 5.45.

Found: N, 8.53; C, 76.16; H, 5.52.

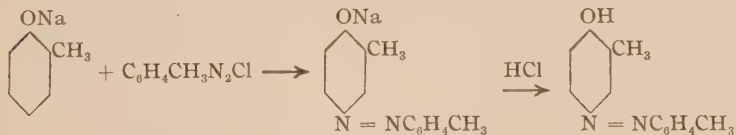
SAPONIFICATION OF TOLUQUINONE- α -BENZOYLPARATOLYLHYDRAZONE.



The saponification represented was effected by dissolving the hydrazone in concentrated sulphuric acid and pouring the resulting solution into a large volume of water. The crude product thus obtained was treated with 20 per cent. caustic potash solution which dissolved the hydroxyazo compound. This was reprecipitated by means of hydrochloric acid, and was then filtered, dried, recrystallized several times from ligroin and thus obtained as orange-yellow crystal clusters melting at 133°. This compound was found to be identical with tolueneazoorthocresol prepared in the manner now to be described.

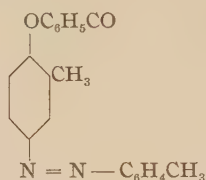
TOLUENEAZOORTHOCRESOL AND ITS BENZOATE.

Tolueneazoorthocresol was prepared⁵⁴ by treating a diazotized solution of paratoluidine with an alkaline solution of orthocresol:



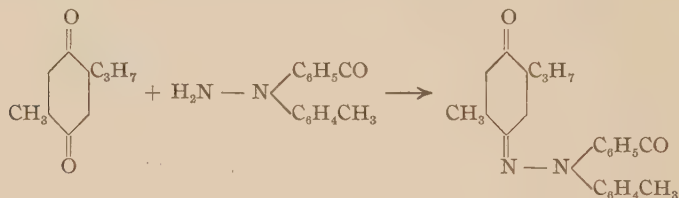
It was purified by dissolving it in a 20 per cent. caustic soda solution precipitating with hydrochloric acid, and subsequent recrystallization from ligroin. Its melting point (135°) was found to be the same as that of the compound obtained by saponifying the toluquinonehydrazone. A mixture of these compounds also melted at 135°. These two compounds are therefore identical.

The benzoate of tolueneazoorthocresol was prepared according to the Baumann-Schöten method. By recrystallizing from ligroin it was obtained in the form of orange-yellow crystal clusters melting at 165°. This compound differs from the hydrazone obtained from toluquinone in color and melting point. The melting point of a mixture of these two compounds is also considerably lower than that of either component. The benzoate must then be represented by the following formula, which shows it to be isomeric with the above-mentioned hydrazone:



THYMOQUINONE- α -BENZOYLPARATOLYLHYDRAZONE.

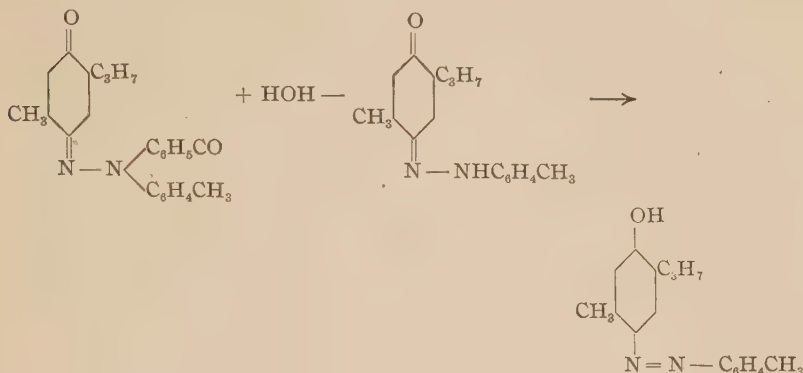
Thymoquinone condenses with the substituted tolylhydrazine as shown in the following equation:



One gram of thymoquinone was dissolved in 300 cc. of 95 per cent. alcohol, the solution diluted to 700 cc. and then treated with a dilute alcoholic solution (3 parts of 95 per cent. alcohol to 4 parts water) containing 3 grams of pure α -benzoylparatolylhydrazine sulphate. After standing 48 hours the solution was filtered and the crude hydrazone (1.5 grams) purified by recrystallizing from ligroin. It was obtained in the form of light yellowish green crystals melting at 125°.

0.4085 gram gave 278 cc. moist N at 20° and 759 mm.
2639 grams gave 0.7475 gram CO₂ and 1567 grams H₂O.

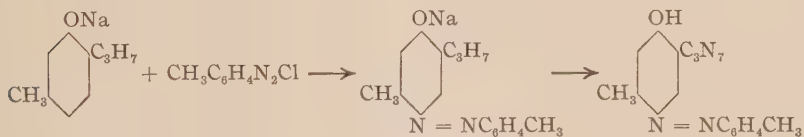
Calculated for C₂₉H₂₄N₂O₂: N, 7.53; C, 77.42; H, 6.45.
Found: N, 7.78; C, 77.25; H, 6.59.

SAPONIFICATION OF THYMOQUINONE- α -BENZOYLPARATOLYLHYDRAZONE.

The saponification indicated was carried out just as described in the case of the benzoquinone hydrazone. The purification was also effected by reprecipitating the compound from alkali solution with hydrochloric acid and recrystallizing from ligroin. The reddish yellow crystals obtained melted at 117° . This compound proved to be identical with tolueneazothymol prepared as described below.

TOLUENEAZOTHYMOL, AND ITS BENZOATE.

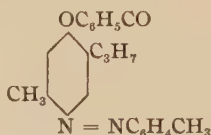
Tolueneazothymol was prepared by a method similar to those used in preparing the other hydroxyazo compounds which have been described. A considerable portion of the solid, which was formed when the diazotized paratoluidine solution was added to the sodium thymolate and the resulting solution neutralized with hydrochloric acid, was found to be insoluble in caustic potash. This was due to the fact that all of the diazo groups did not enter the ring in the para position to the hydroxyl and there was formed, at the same time, a large amount of the orthoazo compound which is insoluble in alkali. Thus the following equation is only a partial representation of the reaction:



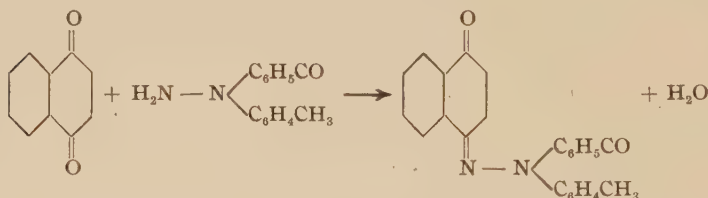
The separation of the para compound from the mixture of the two isomers was accomplished by dissolving the para compound in alkali, filtering from the ortho compound and reprecipitation with hydrochloric acid. It was purified by crystallization from ligroin and ob-

tained as reddish yellow needles melting at 117° . A mixture of this compound and the saponification product of the thymoquinone-hydrazone gave a melting point of 117° and the identity of the two compounds was thus established.

Upon benzoylating the tolueneazothymol according to the Baumann-Schöten method a compound was obtained which crystallized from ligroin in short, red, needle-shaped crystals melting at 126° . A mixture of this compound and thymoquinone- α -benzoylparatolyldiazine melted considerably lower than either constituent. Accordingly, the two compounds must be represented as isomers, the benzoyl derivative of the tolueneazothymol having the following constitution:



PREPARATION OF α -NAPHTHOQUINONEBENZOYLPARATOLYLHYDRAZONE.

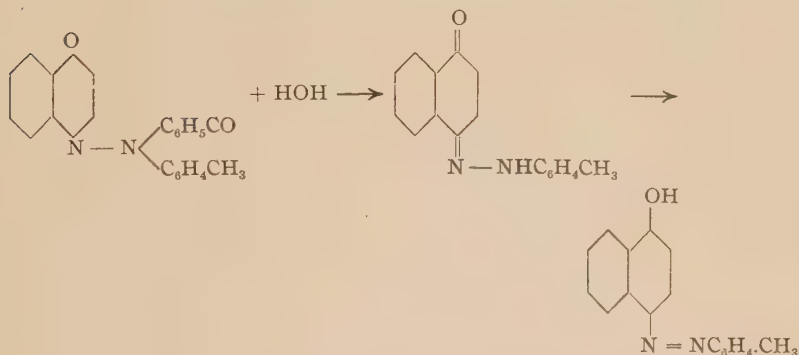


It was expected that the condensation represented above could be effected in the same way as the previously described condensation methods which were used in the preparation of the other hydrazones. A reaction did take place under these conditions but the substance which separated out was a dark red, semi-solid mass which adhered to the inside of the vessel and often changed into a tarry liquid when the solution was poured off. It was found impossible to purify this substance by recrystallization. Repeated experiments using alcoholic solutions of different concentration resulted in obtaining a small amount of the comparatively pure compound. In one experiment 0.2 gram of the compound was obtained when solutions of the following concentration were used: 0.5 gram of α -naphthoquinone was dissolved in 200 cc. of 95 per cent. alcohol and the solution diluted to 500 cc. To this was added 500 cc. of a dilute alcoholic solution (2 parts of 95 per cent. alcohol and 3 parts water) of α -benzoyltolylhydrazine sulphate (1.5 grams). As soon as any precipitate formed it was removed from the solution by decantation or filtration. The solution remaining was allowed to stand

and again filtered as soon as a precipitate formed. This was continued until no further precipitate was formed in the solution. The yellowish compound obtained in this way was recrystallized from benzene-ligroin. It separated in the form of small nodules of fine yellow crystals which melted at 200° .

The naphthoquinone used in these experiments was made by the oxidation of naphthalene according to the method of Japp.⁵⁷ Attempts were made to prepare it from α -naphthylamine by Clark's method.⁵⁸ In these experiments only a very small amount of the compound was obtained.

SAPONIFICATION OF α -NAPHTHOQUINONEBENZOYLPARATOLYLHYDRAZONE.



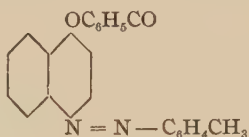
The saponification of the hydrazone would probably take place according to the above equation. Not enough of the compound was obtained, however, to carry out this experiment.

TOLUENEAZONAPHTHOL AND ITS BENZOATE.

Tolueneazonaphthol⁵⁵ was readily formed when a diazotized hydrochloric acid solution of paratoluidine was treated with an alkaline solution of α -naphthol. It crystallized from ligroin, forming very fine, reddish, needle-shaped crystals which melted at 208° . The melting-point determinations of a mixture of this compound and the product of the action of paratolylhydrazine upon α -naphthoquinone showed these compounds to be identical. They are also probably identical with the saponification product of the naphthoquinonebenzoylparatolylhydrazone.

By benzoylating tolueneazonaphthol according to the Baumann-

Schöten method a benzoate of the following constitution was obtained:



This compound crystallized from ligroin in the form of very dark red, metallic crystals which melted at 155° . It is undoubtedly isomeric with α -naphthoquinoneparatolylhydrazone which is yellow in color and melts at 200° .

In conclusion, I wish to thank Professor William McPherson, under whose direction this work was carried out, for his continued interest and helpfulness.

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